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Nitrous oxide emissions from riparian forest buffers, warm-season and cool-season grass filters, and crop fields

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Nitrous oxide emissions from riparian forest buffers, warm-season and cool-season grass filters, and crop fields

Abstract

Denitrification within riparian buffers may trade reduced nonpoint source pollution of surface waters for increased greenhouse gas emissions resulting from denitrification-produced nitrous oxide (N₂O). However, little is known about the N₂O emission within conservation buffers established for water quality improvement or of the importance of short-term N₂O peak emission following rewetting dry soils and thawing frozen soils. Such estimates are important in reducing uncertainties in current Intergovernmental Panel on Climate Change (IPCC) methodologies estimating soil N₂O emission which are based on N inputs. This study contrasts N₂O emission from riparian buffer systems of three perennial vegetation types and an adjacent crop field, and compares measured N₂O emission with estimates based on the IPCC methodology. We measured soil properties, N inputs, weather conditions and N₂O fluxes from soils in forested riparian buffers, warm-season and cool-season grass filters, and a crop field located in the Bear Creek watershed in central Iowa, USA. Cumulative N₂O emissions from soils in all riparian buffers (5.8 kg N₂O-N ha⁻¹ in 2006–2007) were significantly less than those from crop field soils (24.0 kg N₂O-N ha⁻¹ in 2006–2007), with no difference among the buffer vegetation types. While N₂O peak emissions (up to 70-fold increase) following the rewetting of dry soils and thawing of frozen soils comprised 46–70% of the annual N₂O emissions from soils in the crop field, soils in the riparian buffers were less sensitive to such events (3 to 10-fold increase). The ratio of N₂O emission to N inputs within riparian buffers (0.02) was smaller than those of crop field (0.07). These results indicate that N₂O emission from soils within the riparian buffers established for water quality improvement should not be considered a major source of N₂O emission compared to crop field emission. The observed large difference between measured N₂O emissions and those estimated using the IPCC's recommended methodology (i.e., 87% underestimation) in the crop field suggests that the IPCC methodology may underestimate N₂O emission in the regions where soil rewetting and thawing are common, and that conditions predicted by future climate-change scenarios may increase N₂O emissions.

Disciplines

Ecology and Evolutionary Biology | Environmental Indicators and Impact Assessment | Forest Sciences | Soil Science | Sustainability

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Nitrous oxide emissions from riparian forest buffers, warm-season and cool-season grass filters, and crop fields

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Denitrification within riparian buffers may trade reduced nonpoint source pollution of surface waters for increased greenhouse gas emissions resulting from denitrification-produced nitrous oxide (N_2O). However, little is known about the N_2O emission within conservation buffers established for water quality improvement or of the importance of short-term N_2O peak emission following rewetting dry soils and thawing frozen soils. Such estimates are important in reducing uncertainties in current Intergovernmental Panel on Climate Change (IPCC) methodologies estimating soil N_2O emission which are based on N inputs. This study contrasts N_2O emission from riparian buffer systems of three perennial vegetation types and an adjacent crop field, and compares measured N_2O emission with estimates based on the IPCC methodology. We measured soil properties, N inputs, weather conditions and N_2O fluxes from soils in forested riparian buffers, warm-season and cool-season grass filters, and a crop field located in the Bear Creek watershed in central Iowa, USA. Cumulative N_2O emissions from soils in all riparian buffers ($5.8 \text{ kg } \text{N}_2\text{O-N ha}^{-1}$ in 2006–2007) were significantly less than those from crop field soils ($24.0 \text{ kg } \text{N}_2\text{O-N ha}^{-1}$ in 2006–2007), with no difference among the buffer vegetation types. While N_2O peak emissions (up to 70-fold increase) following the rewetting of dry soils and thawing of frozen soils comprised 46–70% of the annual N_2O emissions from soils in the crop field, soils in the riparian buffers were less sensitive to such events (3 to 10-fold increase). The ratio of N_2O emission to N inputs within riparian buffers (0.02) was smaller than those of crop field (0.07). These results indicate that N_2O emission from soils within the riparian buffers established for water quality improvement should not be considered a major source of N_2O emission compared to crop field emission. The observed large difference between measured N_2O emissions and those estimated using the IPCC's recommended methodology (i.e., 87% underestimation) in the crop field suggests that the IPCC methodology may underestimate N_2O emission in the regions where soil rewetting and thawing are common, and that conditions predicted by future climate-change scenarios may increase N_2O emissions.

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1 Introduction

Non-point source (NPS) pollutants such as sediment, nitrogen (N), phosphorus (P) and pesticides are major contributors to water quality problems worldwide (Duda, 1993; Tonderski, 1996; Carpenter et al., 1998). Shortly after the Waikato Valley Authority in New Zealand (1973) first discussed the use of riparian buffers for the prevention of water pollution, a number of research projects were initiated to quantify the ability of riparian buffers to control NPS pollution (e.g. Lowrance et al., 1983; Peterjohn and Correll, 1984). Based on these and other studies, riparian buffers have been recommended as effective tools for coping with NPS pollution (e.g. Mitsch et al., 2001; Sabater et al., 2003; Hubbard et al., 2004).

Important functions of riparian buffers related to NPS pollution control are filtering and retaining sediment, and immobilizing, storing, and transforming chemical inputs from uplands (Schultz et al., 2000). Many studies have shown that riparian buffers can reduce sediment erosion to surface waters by 70 to 95% (e.g. Lee et al., 2000, 2003), N fluxes by 5 to more than 90% (e.g. Kuusemets et al., 2001; Dukes et al., 2002) and P losses by 27 to 97% (e.g. Uusi-Kamppa et al., 2000; Kuusemets et al., 2001). Denitrification is recognized as the major mechanism for reducing nitrate (NO_3^-) within riparian systems, with removal generally ranging from 2–7 g N m⁻² y⁻¹ (e.g.; Groffman and Hanson, 1997; Watts and Seitzinger, 2000).

It recently has been hypothesized that increased denitrification within riparian areas may trade a water quality concern for an atmospheric concern (Groffman et al., 1998), resulting from the greenhouse effect of N₂O produced during nitrification and denitrification (Wang et al., 1976) and its contribution to ozone depletion (Crutzen, 1970; Liu et al., 1977). The global warming potential of N₂O is 298 times that of carbon dioxide (CO₂) and 25 times that of methane (CH₄) in a 100-year time horizon (Forster et al., 2007). Some studies (Groffman et al., 1998, 2000; Hefting et al., 2003, 2006) have concluded that N transformation within riparian buffers with high NO_3^- loads results in a significant increase of greenhouse gas emission. As a result, Groffman et al. (2002)

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suggested that the Intergovernmental Panel on Climate Change (IPCC) inventory might be improved by including additional measurements of riparian N_2O fluxes.

5 Numerous studies have emphasized the role of vegetation in soil biogeochemical processes within riparian buffers. However, there are conflicting results regarding the relationship between vegetation type and denitrification rate in riparian buffers. While some studies (e.g. Hubbard and Lowrance, 1997; Verchot et al., 1997) found higher groundwater NO_3^- removal or denitrification rates in forested riparian zones, other studies (Groffman et al., 1991; Schnabel et al., 1996) found higher removal in grass dominated riparian sites. Some studies (e.g. Hefting et al., 2003; Dhondt et al., 2004) found
10 no significant difference in groundwater NO_3^- removal or denitrification rate between forested and grass-dominated riparian sites. Simpkins et al. (2002) emphasized the importance of hydrogeologic setting and suggested that denitrification would be favored by hydrogeologic conditions of groundwater flow toward the creek, small groundwater velocities, and long groundwater residence times in fine-textured materials. This variability suggests that there are uncertainties about the relationship between the type of perennial vegetation within riparian buffers and soil N_2O emission and illustrates the need for additional studies in various regions of the country, in different landscape settings, and under different vegetation communities to quantify the emission of N_2O from soils in riparian buffers established or managed for water quality functions (Walker et al., 2002).
20

Numerous studies have observed increased soil N_2O emission following wetting of dry soil in tropical grass lands (Nobre et al., 2001), semiarid pasture (Saetre and Stark, 2005), Mediterranean grassland and oak forest (Fierer and Schimel, 2002), dry tropical forests (García-Méndez et al., 1991; Davidson et al., 1993), savanna (Scholes et al., 1997), agricultural lands (e.g. Kusa et al., 2002; Mikha et al., 2005) and in laboratory studies (e.g. Appel, 1998; Hütsch et al., 1999). The increased rates ranged
25 from 5-fold up to 1000-fold (e.g. Prieme and Christensen, 2001; Saetre and Stark, 2005) and magnitudes of the episodic N_2O emission increase varied depending on soil texture (Appel, 1998; Austin et al., 2004), soil water content (Appel, 1998), root

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responses (Cui and Caldwell, 1997), amount of added water (Ruser et al., 2006) and the characteristics and availability of substrates (e.g. Van Gestel et al., 1993; Schaeffer et al., 2003). Based on these studies, it is apparent that even a single wetting event could account for a large proportion of annual emission of N₂O (e.g. Prieme and Christensen, 2001; Nobre et al., 2001). Thawing frozen soils can also lead to increased N₂O emission (e.g. Herrmann and Witter, 2002; Müller et al., 2003). Although the duration of such elevated emission is limited mostly to a few days, these episodes have been found to be an important source of the total annual emission from agricultural land (e.g. Wagner-Riddle and Thurtell, 1998; Teepe et al., 2004), forests (e.g. Papen and Butterbach-Bahl, 1999; Teepe et al., 2000), and grasslands (Kammann et al., 1998). Matzner and Borken (2008) observed that the emission of N₂O after thawing frozen soils was in some cases significantly larger from arable soils than from forest soils. Such events usually occurred at soil temperatures near 0°C (e.g. Chen et al., 1995; Müller et al., 2003). Matzner and Borken (2008) stated that the increase in N₂O emission after thawing increases with colder temperatures of frozen soil. In temperate regions, observed N₂O emissions during freeze-thaw periods in spring may account for up to 70% of the total yearly N₂O emission (e.g. Teepe et al., 2000; Regina et al., 2004).

The Intergovernmental Panel on Climate Change (IPCC) Tier 1 methodology (2006) estimates soil N₂O emission by multiplying N inputs by an emission factor in crop fields, assuming that these N inputs are a source of N₂O. However, estimating N₂O emissions by such N input-based methodologies do not account for the episodic nature of N₂O emissions, and may underestimate fluxes in the regions with frequent rewetting of dry soils and thawing of frozen soils. Therefore, studies assessing the contribution of peak emissions to annual N₂O emissions and evaluating the current IPCC methodology are clearly needed to better understand annual N₂O fluxes and the N cycle within these systems.

Objectives of this study were to compare N₂O emissions from riparian buffer systems established for water quality improvement comprised of forest, warm-season grasses,

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and cool-season grasses and an adjacent crop field, and to compare measured N₂O emissions with estimates using the methodology recommended by the IPCC.

2 Materials and methods

2.1 Study site

5 The study area consisted of three forest buffers, three warm-season grass filters, one cool-season grass filter, and one crop field, all located within the riparian zone within the Bear Creek watershed, Story County and Hamilton County, Iowa, United States of America (42° 11' N, 93° 30' W). Bear Creek (total length 56 473 m) is a third order stream with typical discharges of 0.3 to 1.4 m³ s⁻¹. The watershed drains 6810 ha of
10 farmland, with nearly 90% of these acres in a corn-soybean rotation. Located within the Des Moines Lobe subregion of the Western Corn Belt Plains ecoregion (Griffiths et al., 1994), the study area was once a tallgrass prairie ecosystem containing wet prairie marshes and pothole wetlands in topographically low areas and forests along higher order streams. An ongoing objective of the Bear Creek watershed project has
15 been to establish riparian buffers along the upper portions of the watershed as willing landowners and cost-share are identified (Schultz et al., 2004). This has provided a variety of sites of different streamside vegetation and buffer age to utilize in assessing the spatial and temporal variability of riparian buffers in reducing NPS pollution. Forest buffers and warm-season grass filters were previously under row-crop cultivation and
20 the cool-season grass filter was previously under livestock grazing. Tree species include silver maple (*Acer saccharinum* L.), green ash (*Fraxinus pennsylvanica* Marsh.), black walnut (*Juglans nigra* L.), willow (*Salix* spp.), cottonwood hybrids (*Populus* spp.), red oak (*Quercus rubra* L.), and bur oak (*Quercus bicolor* Willd). Shrub species included chokecherry (*Prunus virginiana* L.), Nanking cherry (*Prunus tomentosa* Thunb),
25 wild plum (*Prunus americana* Marsh), red osier dogwood (*Cornus stolonifera* Michx), and ninebark (*Physocarpus opulifolius* Max.). Warm-season grasses included native

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grasses such as switchgrass (*Panicum virgatum*) Indian grass (*Sorghastrum nutans*), and Big Bluestem (*Andropogon gerardi*). Numerous forb species were present, including purple prairie clover (*Petalostemum purpureum*), black-eyed susan (*Rudbeckia hirta*), yellow coneflower (*Ratibida pinnata*), stiff goldenrod (*Solidago rigida*), prairie blazing star (*Liatris pycnostachya*), and others. The cool-season grass buffer was dominated by non-native forage grasses (*Bromus inermis* L., *Phleum pratense* L., and *Poa pratensis* L). Details of the riparian buffer design, placement, and plant species are given in Schultz et al. (1995). The crop field was planted to a corn (*Zea mays* L.) and soybean (*Glycine max* L. Merr.) rotation, with corn in 2006 and soybeans in 2005 and 2007. Pelletized urea ($133.4 \text{ kg N ha}^{-1}$) was applied to the crop field in April 2006, and fall chisel plowing (15–20 cm depth) was conducted in November 2006. Harvested crop yield was $3934.1 \text{ kg dry matter (d.m.) ha}^{-1}$ (soybeans) in 2005 and $10\,419.8 \text{ kg d.m. ha}^{-1}$ (corn) in 2006. The major soil association in the watershed is the Clarion-Webster-Nicolett association with minor areas of Clarion-Storden-Coland, and Canisteo-Okoboji-Nicolett (Dewitt, 1984). The areas used in this study are all located on the same soil mapping unit (Coland) and have similar topography.

2.2 Nitrous oxide flux and environmental factors measurement

Nitrous oxide flux from soils under riparian forest buffers, warm-season and cool-season grass filters, and the crop field were measured weekly from October 2005 through December 2007 (no measurement in mid April to mid May, August, and September to October 2006 in the crop field). Five points were randomly selected in each of the sites for N_2O gas collection and soil sampling. Nitrous oxide flux measurements were conducted at mid-morning using static vented chambers (PVC, 30-cm diameter \times 15 cm tall with vent). Chambers were equipped with a thermometer to measure air temperature within the chambers at the time of sampling. Ten ml of air was sampled from the chamber with a polypropylene syringe at 15 min intervals for 45 min and the gas stored in evacuated glass vials (6 ml, fitted with butyl rubber stoppers) until analysis. Glass vials were prepared by alternately evacuating the vial headspace and

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flushing with helium to remove air. Nitrous oxide concentrations were determined with a gas chromatograph (Model GC17A; Shimadzu, Kyoto, Japan) equipped with a ^{63}Ni electron capture detector and a stainless steel column (0.3175 cm diameter \times 75.54 cm long) packed with Porapak Q (80–100 mesh). Samples were introduced into the chromatograph using an autosampler described by Arnold et al. (2001). Details of the chamber design and GC analysis are given in Parkin and Kaspar (2006). Nitrous oxide flux was calculated from the linear slope of N_2O concentration change over time (Holland et al., 1999). Our estimated minimum detectable flux was $0.175 \text{ g N}_2\text{O-N ha}^{-1} \text{ h}^{-1}$ (Parkin and Kaspar, 2006). Some of the fluxes measured from the individual chambers were smaller than our detection limit. The measured values of these "nondetects" were included in computing mean fluxes (Gilbert, 1987; Chan and Parkin, 2001).

Soil temperature and soil moisture near the chambers were measured simultaneously with N_2O gas collection at a 5 cm depth using a digital thermocouple and a digital soil moisture meter (HydroSense, Campbell Scientific, Inc., Logan, Utah, USA). Air temperature was measured simultaneously with N_2O gas collection inside and outside the gas chamber. Continuous measurements of soil temperature, air temperature, and soil moisture at 5 cm soil depths were collected using a data logger (HOBO Micro station data logger with sensors, Onset Computer Corporation, Bourne, MA USA) at one site per vegetation type. Daily rainfall and snow data were provided by the nearest meteorology station (Colo, IA, $42^\circ 01' \text{ N}$, $93^\circ 19' \text{ W}$) (Herzmann, 2004).

2.3 Diel variation of N_2O flux and Q_{10} relationship

In addition to regular measurements described above, the diel variation in N_2O flux was measured during 21–22 November 2005, 18–19 May 2006, and 16–17 July 2007. For this assessment, three locations were randomly selected for flux measurements within each of the forest buffer, warm-season and cool-season grass filter, and the crop field. Nitrous oxide flux and soil temperature was measured every three hour for 24 h at all sites. To examine soil temperature sensitivity of N_2O flux during the diel measurements,

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we conducted nonlinear regression analyses using $N_2O \text{ flux} = a \times Q_{10}^{(\text{soil temperature}/10)}$ (Q_{10} represents activity increase of N_2O flux for every 10°C increase in soil temperature) (Parkin and Kaspar, 2006).

2.4 Cumulative N_2O flux calculations

- 5 Because fluxes were measured during the day time when soil temperatures were generally higher than the daily average soil temperatures, cumulative N_2O fluxes were calculated using soil-temperature-corrected daily flux measurements (Parkin and Kaspar, 2003, 2006). Temperature corrections were done with a Q_{10} relationship, using the 5 cm soil temperature at the time each flux was measured, along with the daily
- 10 average soil temperature for that day. Daily average N_2O flux was calculated using the equation:

$$\text{Daily Average } N_2O \text{ Flux} = N_2O_{\text{measured}} \times Q^{(DAT-T)/10} \quad (1)$$

- where N_2O_{measured} is measured N_2O flux at a specific hour, T is the soil temperature at the time the flux was measured, DAT is the daily average soil temperature, Q is the Q^{10} factor, and Daily Average N_2O Flux is the resulting estimated daily average flux
- 15 based on the single hourly measured N_2O flux. Cumulative N_2O fluxes were calculated by linear interpolation and numerical integration of daily N_2O fluxes between sampling times.

2.5 Soil sampling and analysis

- 20 Six intact soil cores (5.3 cm diameter) were collected to a depth of 15 cm in each of the forest buffer, warm-season grass filter, cool-season grass filter, and adjacent crop field in October 2006 and September 2007. A plastic sleeve liner was placed inside the metal core tube and the liner with the intact soil core removed from the tube and capped for transport to the laboratory. Soils samples were stored at 4°C until analysis.
- 25 Soil pH was determined using a pH meter (Accument 910, Fisher Scientific Ltd.,

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Pittsburgh, PA, USA) on a 1:1 diluted soil solution. Gravimetric moisture content was determined by oven drying a subsample at 105°C for 24 h and bulk density was determined by the core method (Grossman and Reinsch, 2002). For C and N analysis, soils were air dried at room temperature, sieved (2mm) and gravimetric moisture content determined. Total C (TC) and total N (TN) were measured using a Flash EA 2000 (ThermoFinnigan, Milan, Italy) direct combustion instrument. Soil inorganic N was extracted with 2M potassium chloride (KCl) and stored at 4°C until filtration (within 4 h of field collection of the soil cores) (Van Miegroet, 1995). Filtrates were frozen and stored until analysis. Nitrate and ammonium (NH_4^+) contents were analyzed by colorimetric method (Mulvaney, 1996) with an auto analyzer (Quikchem 8000 FIA+, Lachat Instruments, Milwaukee, WI, USA).

2.6 Nitrogen inputs to sites and ratio of N_2O emission to N inputs

Nitrogen inputs as direct sources of N_2O were estimated in warm-season and cool-season grass filters, a forest buffer and adjacent crop field. Pelletized urea ($133.4 \text{ kg N ha}^{-1}$) was applied in the crop field (corn) in April 2006. Annual dry and wet deposition was $7.7 \text{ kg N ha}^{-1} \text{ y}^{-1}$ on the Iowa State University campus (19 km south of the study site) in January 2003–January 2004 (Anderson and Downing, 2006) and the value was used for N input from deposition in 2006 and 2007. Nitrogen inputs from soybeans residue was estimated from samples collected in five randomly located plots ($50 \text{ cm} \times 50 \text{ cm}$) in the crop field after the harvest of soybeans in 2005. Nitrogen inputs from corn residues (Y_r) in 2006, were estimated using a harvest index (HI, 0.53; from Johnson et al., 2006) and harvested corn yields (Y_{gr} , $10\,419.8 \text{ kg ha}^{-1} \text{ y}^{-1}$) as following:

$$Y_r = Y_{gr}[(1/\text{HI}) - 1] \quad (2)$$

where Y_r is corn residues (kg ha^{-1}), and Y_{gr} is harvested corn grain and HI is harvest index (Johnson et al., 2006).

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N inputs from dead roots in the crop field were calculated from the previous studies on the same sites (Tufekcioglu et al., 1999 and 2003). Biological N fixation was not included as a direct source of N_2O because of the lack of evidence of significant emissions arising from the fixation process itself (Rochette and Janzen, 2005; IPCC, 2006).

N inputs from litter-fall within a forest buffer was estimated from monthly samples collected within five litter-fall collecting baskets (50 cm × 50 cm) placed at random locations within the forest buffer starting in September 2005. In addition, above-ground biomass was harvested within five randomly located plots (50 cm × 50 cm) in the warm-season and cool-season grass filters, and the forest buffer in early November of 2005 and 2006. Samples were dried (70°C, 48 h), weighed, and stored for TN analysis. Total N was measured by direct combustion using a Flash EA 2000 (ThermoFinnigan, Milan, Italy). N inputs from dead roots in warm-season and cool-season grass filters, and the forest buffer were calculated from previous studies conducted within the same sites (Tufekcioglu et al., 1999, 2003). In these same sites, Lee et al. (2003) estimated that 0.5 kg N transported from crop fields in run-off was retained in the riparian buffers per an event (>20 mm rainfall) and there were 13 events exceeding this threshold during 2006–2007. Based on these data, N input from runoff to riparian buffers was estimated in 2006 and 2007, respectively. Nitrogen input from groundwater discharged from crop fields to the riparian buffers was estimated by averaging lost N load in groundwater measured in wells under two of the riparian buffers (Kim et al., 2009). Using the cumulative annual N_2O emission and N input in the sites, the ratio of N_2O emission to N inputs (N_2O emission factor, EF) in the crop field and riparian buffers was determined.

2.7 Watershed-scale estimation of N_2O emission

Nitrous oxide emission from all cropped fields within the Bear Creek watershed was estimated by multiplying the determined N input and N_2O emission factor (EF_{CF}) in the crop field, by area of the crop fields (6810 ha). The equation for estimating N_2O

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emission from whole crop fields is:

$$N_2O - N_{CF} = (\text{Fertilizer N} + \text{Crop residues N} + \text{N deposition}) \times EF_{CF} \times \text{Area}_{CF} \quad (3)$$

where N_2O-N_{CF} is annual direct N_2O-N emissions from N inputs to crop fields ($\text{kg } N_2O-N y^{-1}$); Fertilizer N is annual amount of synthetic fertilizer N applied to soils ($\text{kg N ha}^{-1} y^{-1}$); Crop residues N is amount of N in crop residues (above- and below-ground), including N-fixing crops returned to soils ($\text{kg N ha}^{-1} y^{-1}$); N deposition is N in dry and wet deposition; EF_{CF} is emission factor for N_2O emissions from N inputs in crop fields ($\text{kg } N_2O-N (\text{kg N input})^{-1}$); and Area_{CF} is area of crop fields in the Bear Creek watershed (6810 ha).

Nitrous oxide emission from riparian buffers already re-established in the watershed was estimated by applying measured areal emissions [N input and N_2O emission factor (EF_{RB})] from study sites to the total area of established riparian buffers (75.9 ha). To estimate N_2O emission from hypothetical riparian buffers established for water quality improvement throughout the watershed, it was assumed that both sides of the creek (56 473 m) would be bordered by 30 m width riparian buffers (current design criteria, Mayer et al., 2006). The equation for estimating N_2O emission from riparian buffers is:

$$N_2O - N_{RB} = (\text{Litter and roots N} + \text{Run off N} + \text{Groundwater N} + \text{N deposition}) \times EF_{RB} \times \text{Area}_{RB} \quad (4)$$

where N_2O-N_{RB} is annual direct N_2O-N emissions from N inputs to riparian buffers ($\text{kg } N_2O-N y^{-1}$); Litter and roots N is annual amount of N in litter-fall and dead roots ($\text{kg N ha}^{-1} y^{-1}$); Run off N is amount of N in run off from crop fields ($\text{kg N ha}^{-1} y^{-1}$); Groundwater N is N in groundwater exported to riparian buffers from crop fields ($\text{kg N ha}^{-1} y^{-1}$); N deposition is N in dry and wet deposition ($\text{kg N ha}^{-1} y^{-1}$); EF_{RB} is emission factor for N_2O emissions from N inputs in riparian buffers ($\text{kg } N_2O-N (\text{kg N input})^{-1}$); and Area_{RB} is area of riparian buffers.

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2.8 Intergovernmental Panel on Climate Change N₂O flux calculations

The Intergovernmental Panel on Climate Change (IPCC) Tier 1 methodology (2006) separately estimates direct N₂O emission (i.e. directly from the soils to which N is added/released) and indirect N₂O emission resulting from offsite N movement (i.e. volatilization of NH₃ and NO_x, and leaching and runoff of N) from managed soils. The method then estimates direct N₂O emission from crop fields by multiplying N inputs by an emission factor. For this study, N inputs from synthetic fertilizer (F_{SN}) and crop residues (F_{CR}) estimated as described above were summed and multiplied by an emission factor (EF₁). The equation for estimating direct N₂O emission is:

$$N_{2O_{Direct}} - N = N_{2O} - N_{Ninputs} = (F_{SN} + F_{CR})EF_1 \quad (5)$$

where N_{2O_{Direct}}-N is annual direct N₂O-N emissions produced from managed soils (kg N₂O-N y⁻¹); N₂O-N_{Ninputs} is annual direct N₂O-N emissions from N inputs to managed soils (kg N₂O-N y⁻¹); F_{SN} is annual amount of synthetic fertilizer N applied to soils (kg N y⁻¹); F_{CR}=amount of N in crop residues (above- and below-ground), including N-fixing crops returned to soils (kg N y⁻¹); and EF₁ is emission factor for N₂O emissions from N inputs (kg N₂O-N (kg N input)⁻¹). The IPCC default value for EF₁ is 0.01. Details of calculating F_{CR} is given in IPCC (1997, 2006).

The IPCC (2006) Tier 1 estimates N₂O emission from atmospheric deposition of N volatilized from crop fields (indirect N₂O emission) by multiplying N inputs (F_{SN}) by a fraction factor (EF₄) for volatilized N. Because synthetic fertilizer is an N input potentially volatilized in the crop fields, the equation for estimating N₂O emission is:

$$N_{2O_{(ATD)}} - N = (F_{SN} \times \text{Frac}_{GASF}) \times EF_4 \quad (6)$$

where N_{2O_(ATD)}-N is annual amount of N₂O-N produced from atmospheric deposition of N volatilized from managed soils (kg N₂O-N y⁻¹); F_{SN} is annual amount of synthetic fertilizer N applied to soils (kg N y⁻¹); Frac_{GASF} is fraction of synthetic fertilizer N that volatilizes as NH₃ and NO_x [kg N volatilized (kg of N applied)⁻¹, IPCC default value

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0.10 for $\text{Frac}_{\text{GASF}}$]; and EF_4 is emission factor for N_2O emissions from atmospheric deposition of N on soils and water surfaces [$\text{kg N-N}_2\text{O} (\text{kg NH}_3\text{-N} + \text{NO}_x\text{-N volatilized})^{-1}$, IPCC default value for EF_4 is 0.010].

2.9 Statistical analyses

5 Normality of the distribution of the data was analyzed using the Shapiro-Wilk normality test. One-way analysis of variance (ANOVA) was used to evaluate the differences in soil properties, and diel and seasonal N_2O flux by site. When the standard assumptions of normality were violated, non-parametric Kruskal-Wallis one-way ANOVA on ranks was used. Differences were considered significant at the $P<0.05$ level. To determine
10 the relationship between soil properties and N_2O flux, correlation analysis using the GLM procedure was applied and NONLIN procedure was utilized for deriving the best fit of N_2O flux models developed by the relationship between soil temperature and N_2O flux. These statistical analyses were conducted by SAS version 8.1 (SAS institute, 1999).

15 **3 Results**

3.1 Soil properties and periods dried and frozen soil

Soil texture was loam at all sites (Marquez et al., 2004). Soils within the forest buffer and warm and cool-season grass filters had significantly (one-way ANOVA) lower bulk density, higher pH, TC, TN, and NH_4^+ than crop fields, while soil NO_3^- was not significantly
20 different among sites (Table 1).

Soils had longer dry (soil moisture $<15\%$) and frozen (soil temperature $<0^\circ\text{C}$) periods in 2007 than in 2006 (Fig. 4D and E). From 15 June to 15 August 2006 (93 d), soils (5 cm depth) were extremely dry ($<15\%$) within crop fields for 12 days, within forest buffers 0 days, and within grass filters 51 days. In comparison, from 15 June to 15

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August 2007 (93 d), soils were extremely dry (<15%) within crop fields for 78 days, within forest buffers for 32 days, and within grass filters for 24 days. From January to March 2006 (90 days), soils (5 cm depth) were frozen (<0°C) within the crop field for 47 days, within forest buffers for 17 days, and within grass filters for 49 days. In comparison, from January to March 2007 (90 days), soils were frozen (<0°C) within the crop field for 82 days, within forest buffers for 46 days, and within grass filters for 62 days.

3.2 Diel variation of N₂O flux and cumulative diel N₂O emission

Diel variation of N₂O flux and soil temperature in the crop field and riparian buffers are shown in Fig. 1. During the 21–22 November 2005, there was no significant difference in N₂O flux between the crop field and riparian buffers (one-way ANOVA $P=0.395$) and also no significant correlation between soil temperature (5 cm depth, 2–5°C) and N₂O flux in the crop field and riparian buffers during this late fall period (all $P>0.05$). In contrast, N₂O flux in the crop field was significantly higher than riparian buffers in both 18–19 May 2006 (7 to 13 times, Kruskal-Wallis one-way ANOVA $P<0.001$) and 16–17 July (12 to 18 times, Kruskal-Wallis one-way ANOVA $P<0.001$), but there were no differences among vegetation types in riparian buffers in the both periods (Tukey's Studentized Range Test) (Fig. 1). Significant correlations between soil temperature (5 cm depth) and N₂O flux were only found within the crop field during 18–19 May 2006 (Pearson coefficient $r=0.77$ $P=0.02$) and 16–17 July 2007 (Pearson coefficient $r=0.48$ $P=0.02$). The resulting Q₁₀ models (N₂O flux = $a \times Q_{10}^{(\text{soil temperature}/10)}$) and Q₁₀ factors were:

May 2006 (soil temperature 11–17°C, crop field):

$$\text{N}_2\text{O flux (mg N}_2\text{O-N ha}^{-1} \text{ h}^{-1}) = 28.9 \times 12.28^{(\text{soil temperature}/10)} (R^2=0.67)$$

Q₁₀ factor 12.78

July 2007 (soil temperature 23–27°C, crop field):

$$\text{N}_2\text{O flux (mg N}_2\text{O-N ha}^{-1} \text{ h}^{-1}) = 411.0 \times 2.27^{(\text{soil temperature}/10)} (R^2=0.87)$$

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Q₁₀ factor 2.27

Cumulative diel N₂O emissions from the crop field during the three measured dates was 5.9 g N₂O-N ha⁻¹ d⁻¹ during 21–22 November 2005, 43.2 g N₂O-N ha⁻¹ d⁻¹ during 18–19 May 2006, and 130.3 g N₂O-N ha⁻¹ d⁻¹ during 16–17 July 2007 (Fig. 2). In contrast, the range of cumulative diel N₂O emissions from the riparian buffers during the three measured dates was 1.0–3.0 g N₂O-N ha⁻¹ d⁻¹ during 21–22 November 2005, 3.9–6.0 g N₂O-N ha⁻¹ d⁻¹ during 18–19 May 2006, and 7.1–10.5 g N₂O-N ha⁻¹ d⁻¹ during 16–17 July 2007 (Fig. 2). When compared, N₂O emissions from the crop field were 2 to 5-fold higher than riparian buffers during 21–22 November 2005, 7 to 11-fold higher during 18–19 May 2006, and 12 to 14-fold higher during 16–17 July 2007 (Fig. 2).

3.3 Seasonal variation of N₂O flux and cumulative N₂O emission

When assessed seasonally, N₂O flux in the crop field was significantly correlated with air temperature (Pearson coefficient $r=0.38$ $P=0.0001$), soil temperature (5 cm depth) ($r=0.42$ $P<0.0001$) and soil moisture (5 cm depth) ($r=0.35$ $P=0.005$). In all riparian buffers, N₂O flux was significantly correlated with air temperature (Pearson coefficient $r=0.1–0.5$ $P<0.01$) and soil temperature (5 cm depth) ($r=0.3–0.6$ $P<0.0001$) during this same period. The average of observed N₂O fluxes in the crop field (39.4 ± 7.1 kg N₂O-N ha⁻¹ d⁻¹, $n=76$) was significantly higher than in riparian buffers ($2.8–11.0$ kg N₂O-N ha⁻¹ d⁻¹, $n=72–93$) ($P<0.0001$), but there were no differences among riparian buffer vegetation types (Tukey's Studentized Range Test) (Fig. 3).

Q₁₀ factors used for correcting daily average N₂O flux in the crop field were distinguished for three different field soil temperature ranges (<10°C, 10–20°C, >20°C) as follows:

- (1) soil temperature <10°C condition; no valid Q₁₀ factor, Measured N₂O Flux=Diel average N₂O Flux
- (2) soil temperature 10–20°C condition; Q₁₀ factor 12.78 was applied
- (3) soil temperature >20°C condition; Q₁₀ factor 2.27 was applied

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Since there was no significant effect of soil temperature on diel N_2O flux (no valid Q_{10} factor) in the forest buffer, and warm-season and cool-season grass filters, measured N_2O flux was used as a diel average N_2O flux.

5 In both 2006 and 2007, annual cumulative N_2O emission was significantly greater in the crop field ($7.2 \text{ kg N}_2\text{O-N ha}^{-1}$ in 2006 and $16.8 \text{ kg N}_2\text{O-N ha}^{-1}$ in 2007) than in forest buffers ($1.8 \text{ kg N}_2\text{O-N ha}^{-1}$ in 2006 and $4.5 \text{ kg N}_2\text{O-N ha}^{-1}$ in 2007) and grass filters ($1.8 \text{ kg N}_2\text{O-N ha}^{-1}$ in 2006 and $3.4 \text{ kg N}_2\text{O-N ha}^{-1}$ in 2007) (Table 3). The annual cumulative N_2O emission in the crop field, forest buffers, and grass filters in 2007 were 2 to 2.5-fold larger than 2006.

10 3.4 N_2O peak emission

Several periods of peak N_2O emission contributed significantly to annual N_2O emission in both the crop field and riparian buffers (Fig. 4A and B). In the crop field 2006, two large peak emissions following the thawing of frozen soil (13-fold increase, February) and rewetting of dry soil (37-fold increase, November) contributed 33.8% of the annual N_2O emission. In the crop field during 2007, a peak emission followed the thawing of frozen soil (28-fold increase, March) and three peak emissions followed rewetting of dry soil (5 to 70-fold increase, July to October). These four peak emissions contributed 70.3% of annual N_2O emission. All of the peak emissions returned to lower levels within a week. In warm-season and cool-season grass filters during 2006, two peak emissions (July and December) followed the rewetting of dry soil, and contributed 17.0% of annual N_2O emission. In grass filters during 2007, a peak emission after the thawing of frozen soil (March) and two peak emissions after rewetting of dry soil (June and December) contributed 31.1% of the annual N_2O emission. In forest buffers during 2006, a peak emission after the rewetting of dry soil (July) contributed 10.8% of annual N_2O emission, and in 2007, a peak emission after the thawing of frozen soil (March) and two peak emissions after rewetting of dry soil (June and December) contributed 70.5% of annual N_2O emission. Across all vegetation types, N_2O peak emissions were

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3 to 10-fold greater than base-line levels after the thawing of frozen soil or rewetting of dry soil and the peaks returned to lower levels within a week. Soils within the crop field showed higher peak rates of N_2O emission than riparian buffers in both 2006 and 2007. As a result, the contribution of peak emissions to annual N_2O emission was larger in the crop field than in riparian buffers during both years, with the contribution higher in 2007 than 2006.

Several negative N_2O fluxes were observed in the crop field and riparian buffers (Fig. 5). There were no significant differences among sites ($P=0.99$) and the negative fluxes showed no significant relation to soil or air temperature or soil moisture ($P>0.05$). The negative N_2O fluxes were most frequently observed (81%) in the less than 5°C soil temperature range, and the observed maximum negative N_2O flux was $-0.64 \text{ g N}_2\text{O-N ha}^{-1} \text{ h}^{-1}$ ($-64.0 \mu\text{g N}_2\text{O-N m}^{-2} \text{ h}^{-1}$) (Fig. 5). The negative N_2O fluxes observed were insignificant in the overall N_2O fluxes.

3.5 Nitrogen inputs and ratio of N_2O emission to N inputs

In 2006, N fertilizer ($133.4 \text{ kg N ha}^{-1}$) applied in the crop field (corn) resulted in a larger N input to the crop field than riparian buffers. However, in 2007, N input to the crop field was less than riparian buffers, mainly due to no fertilizer application. Nitrogen input from crop residues and dead roots in the crop field was 82.1 and $92.2 \text{ kg N ha}^{-1}$ in 2006 and 2007, respectively (Tables 2 and 3). Annual dry and wet deposition was 7.7 kg N ha^{-1} in the crop field and riparian buffers. Total N inputs in the crop field were $323.1 \text{ kg N ha}^{-1}$ through 2006 and 2007 (Table 3).

Nitrogen input from plant litter and dead roots within riparian buffers was estimated at 83.6 in 2006 and $69.0 \text{ kg N ha}^{-1}$ in 2007 (Table 2). N input from runoff to riparian buffers was estimated at 0.5 in 2006 and 6.0 kg N ha^{-1} in 2007. Nitrogen input from groundwater discharged from the crop field to the riparian buffers was $36.1 \text{ kg N ha}^{-1}$ in 2006 and 2007. Total N inputs in riparian buffer was $246.7 \text{ kg N ha}^{-1}$ through 2006 and 2007 (Table 3) which is 23.6% less than crop field inputs.

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The ratio of measured N₂O emission to N inputs to soils in the crop field in 2006 (0.03) was 3-fold higher than the ratio of riparian buffers in 2006 (0.01) (Table 3). In 2007, the ratio of measured N₂O emission to N inputs to soils in the crop field (0.17) was over 5-fold higher than to riparian buffers (0.03) (Table 3). Overall, the ratio of measured N₂O emission to N inputs to soils in the crop field (0.07) was over 3-fold higher than the ratio of riparian buffers (0.02) (Table 3).

3.6 Watershed-scale estimation of N₂O emission

The estimated total N₂O emission from all cropped fields within the Bear Creek watershed was 77 010.9 kg N y⁻¹ compared to 187.2 kg N y⁻¹ for actual riparian buffers and 835.9 kg N y⁻¹ for hypothetical riparian buffers (Table 4). The resulting estimated ratio of N₂O emission from all cropped fields to N₂O emission in current and hypothetical riparian buffers in the watershed would be 0.002 and 0.01, respectively (Table 4).

3.7 Comparison of measured N inputs and N₂O emission with estimated values by IPCC method

Estimated N input from crop residues and dead roots in the crop field by IPCC method (2006) was 56.4 in 2006 and 118.3 kg N ha⁻¹ in 2007 (Table 2). Compared to the measured N input values (Table 2), the IPCC method underestimated inputs by 31% in 2006 and overestimated inputs by 28% in 2007 in the crop field. In the crop field, estimated N₂O emission (by IPCC 2006) was 2.0 kg N ha⁻¹ in 2006 and 1.2 kg N ha⁻¹ in 2007 (Table 3). The ratio of measured N₂O emission to estimated N₂O emission in the crop field was 3.5 in 2006 and 14.2 in 2007, with an overall ratio of 7.5 for both years (Table 3) indicating that the IPCC method underestimated N₂O emission about 87% in the crop field.

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4 Discussion

4.1 N₂O emission from cropped fields and riparian buffers

In our studies, measured N₂O emissions from soils within all riparian buffers (1.8–4.0 kg N₂O-N ha⁻¹ y⁻¹) were significantly lower than within the crop field (7.2–16.8 kg N₂O-N ha⁻¹ y⁻¹) and there were no observed differences in N₂O emissions among the different riparian buffer vegetation types (Fig. 3). Other studies (Weller et al., 1994; Groffman et al., 1998; Machefert et al., 2004) have measured 0.1–5.3 kg N ha⁻¹ y⁻¹ of N₂O emissions from soils within riparian buffers, similar to observations within this study. In similar studies within temperate regions, mean N₂O emissions measured within fertilizer-applied grassland were 8.0±1.4 kg N₂O-N ha⁻¹ y⁻¹, within grassland without fertilizer were 1.4±0.4 kg N₂O-N ha⁻¹ y⁻¹, and within forests were 0.7±0.3 kg N₂O-N ha⁻¹ y⁻¹ (Stehfest and Bouwman, 2006). Nitrous oxide emissions from soils within riparian buffers in 2006 (1.8 kg N₂O-N ha⁻¹ y⁻¹) in our studies were similar to N₂O emission from soils in unfertilized grass lands and forest in temperate regions. This suggests that N₂O emissions from soils within riparian buffers established to perennial vegetation for water quality functions were similar to those from natural ecosystem.

When scaled to the watershed level, the ratio of estimated N₂O emissions from all cropped fields within the Bear Creek Watershed to N₂O emissions from actual and hypothetical riparian buffers in the watershed would be 0.002 and 0.01, respectively (Table 4). Since dissolved N₂O emission in groundwater leached from the crop fields was negligible in comparison to soil N₂O emission in the crop fields (ratio between dissolved N₂O emission and soil N₂O emission, 0.0003) (Kim et al., 2009), this suggests that the contribution of N₂O emission from riparian buffers to total N₂O emission in the watershed may be around 1%, even if riparian buffers are extended along both sides of the entire creek in the watershed to maximize water quality benefits. Weller et al. (1994) estimated 0.35 kg N ha⁻¹ and 0.04 kg N ha⁻¹ of annual N₂O loss in soil emis-

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sion and groundwater (<1% of the intercepted N) in riparian buffers and concluded N_2O production in the riparian buffers is neither an important fate of N removed from cropland discharges nor an important source of atmospheric N_2O pollution. Similarly, Dhondt et al. (2004) observed N_2O emissions of -0.6 to $2.5 \text{ mg N}_2\text{O-N m}^{-2} \text{ d}^{-1}$ in three NO_3^- loaded riparian sites and concluded the observed N_2O emission did not represent a transfer from water pollution to greenhouse gas emission. Teiter and Mander (2005) reported that N_2O emissions from the riparian gray alder stand which varied from -0.4 to $58 \mu\text{g N}_2\text{O-N m}^{-2} \text{ h}^{-1}$ and concluded that the global warming potential of the riparian alder forest from N_2O was relatively low. Our results, along with those of past studies, suggest that the riparian buffers, even when established to promote denitrification, should not be considered a major source of N_2O emission in the watershed.

In contrast, some studies (Walker et al., 2002; Hefting et al., 2003) have shown much higher N_2O emission from soils within riparian areas. Walker et al. (2002) observed that N_2O emission in a recovering riparian zone and a grazed riparian zone was $24.19 \text{ kg N ha}^{-1} \text{ y}^{-1}$ and $24.50 \text{ kg N ha}^{-1} \text{ y}^{-1}$, respectively. Hefting et al. (2003) observed that N_2O emissions were significantly higher in the forested buffer system ($20 \text{ kg N ha}^{-1} \text{ y}^{-1}$) than within the grassland buffer zone ($2\text{--}4 \text{ kg N ha}^{-1} \text{ y}^{-1}$). They suggested that the higher rates of N_2O emissions within the forested buffer zone were associated with higher NO_3^- concentration in the groundwater, and that N transformation by buffer zones with high NO_3^- loading resulted in a significant increase of N_2O emission. This is consistent with the work of Ullah and Zinati (2006) who reported that prolonged N loading resulted in higher N_2O emissions in riparian forest soils compared to emission rates from non-exposed forest soils. Hefting et al. (2006) reported that locations with high NO_3^- removal efficiency also contribute significantly to increased N_2O emission from riparian zones.

Considering all of these results, it is likely that N_2O emission from riparian buffers is highly site specific and may vary with site characteristics such as soil type, magnitude and speciation of N input, and hydrologic characteristics (Walker et al., 2002). In our study, lower N inputs and fewer N_2O peak emissions observed within in riparian buffers

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result in less N_2O emission than adjacent crop field and compared to several other studies (Walker et al., 2002; Hefting et al., 2003).

The magnitude and frequency of the episodic N_2O emissions observed in our studies indicate the importance of frequent measurements to reduce the uncertainty of longer-term N_2O flux measurements and may partially explain the differences in results from previous. For example, the N_2O emission value reported by Walker et al. (2002) was determined with three month measurements for 14 months. Hefting et al. (2003) and Dhondt et al. (2004) measured N_2O emission in February, May, August, and November representing winter, spring, summer and fall seasons. Teiter and Mander (2005) measured N_2O emission once a month for 15 months through three years and Hefting et al. (2006) measured N_2O emission once in winter and once in summer to obtain the difference of N_2O emission in high and low NO_3^- removal transects. Several other studies have also shown that annual N_2O flux is significantly increased by episodic events such as rewetting of dry soil and thawing of frozen soil as well as N input (e.g. Müller et al., 2003; Mikha et al., 2005) and the peak N_2O emission substantially contribute to total N_2O emission (e.g. Prieme and Christensen, 2001; Nobre et al., 2001). It is important that future studies consider the implications of such episodic events for flux-measurement protocols (Parkin, 2008).

4.2 Peak N_2O emissions

In the crop (soybeans) field in 2007, even though N inputs were less than the crop (corn) field 2006 because N fertilizer was not applied, both annual N_2O emission ($16.8 \text{ kg N}_2\text{O-N ha}^{-1} \text{ y}^{-1}$) and the EF (0.17) were larger than the crop field 2006 (annual N_2O emission: $7.2 \text{ kg N}_2\text{O-N ha}^{-1} \text{ y}^{-1}$, EF: 0.03) (Table 3). In the same region of central Iowa, Parkin and Kasper (2006) observed annual N_2O emission from soybeans fields of $2.2\text{--}2.7 \text{ N}_2\text{O-N ha}^{-1} \text{ y}^{-1}$ and corn fields (N fertilizer 215 kg N ha^{-1}) of $7.6\text{--}10.2 \text{ N}_2\text{O-N ha}^{-1} \text{ y}^{-1}$. Our N_2O emission estimate from the crop field in 2006 is similar to these authors' observation under corn; however, our emission estimate from

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the crop field in 2007 when soybeans were present is 6 to 7- fold higher than Parkin and Kasper's (2006) observation. The N₂O emission from the crop field in 2007 is also larger than average N₂O emission observed in the crop fields in temperate regions observed by Stehfest and Bouwman (2006) of $3.6 \pm 0.5 \text{ kg N}_2\text{O-N ha}^{-1} \text{ y}^{-1}$. The emission factor in the crop field 2007 is also larger than other reports (Bouwman et al., 2002; Stehfest and Bouwman, 2006; Novoa and Tejeda, 2006) and the IPCC (2006)'s default value (0.01, uncertainty range 0.003–0.03). A similar pattern was also observed within soils within riparian buffers in 2007. These results indicate that N₂O emission from soils within the crop field and riparian buffers were caused by additional factors beyond N inputs. One such factor may be the peak N₂O emissions observed within the crop field and riparian buffers during each year. There were several peak emissions following rewetting dry soils and thawing frozen soils in both sites (Fig. 4), and the peak emissions significantly contributed (30-70%) to the amount of annual N₂O emission. This result is consistent with other studies (e.g. Teepe et al., 2000; Prieme and Christensen, 2001; Nobre et al., 2001; Regina et al., 2004) reporting peak N₂O emissions following rewetting dry soils and thawing frozen soils contributed substantially to annual N₂O emissions. In our sites, we observed that the crop field had N₂O peak emissions of greater magnitude than riparian buffers (Fig. 3). This result is similar to studies reviewed by Matzner and Borken (2008) in that the emissions of N₂O after thawing frozen soils were sometimes significantly larger from arable soils than from forest soils. In our observations, soils within the crop field had lower soil temperatures in winter and higher soil temperature and longer dry periods in summer compared with soils within riparian buffers (Fig. 4D, E). This may explain why peak emissions during periods of rewetting and thawing were higher in the crop field than riparian buffers. Vegetation within riparian buffers provides more shade, preventing high temperature increases during the summer months and provides insulation, preventing severe temperature decreases during winter months. In contrast, soils within the crop field are exposed to direct sunlight during the summer months and cold wind during the winter months. Riparian vegetation will also result in lower soil bulk density and higher

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organic matter (Marquez et al., 1999; Tufekcioglu et al., 2001; Bharati et al., 2002), resulting in higher soil moisture. In contrast, soils within the crop field exposed to direct sunlight, with higher bulk density, and lower soil organic matter will tend to hold less soil moisture compared with riparian buffer soils. We observed that the contribution of peak emissions to annual N₂O emission was larger in 2007 than 2006 in both the crop field and riparian buffers. The period soils were frozen during winter months and the period soil were dried during summer months were longer in 2007 compared with 2006, and this may explain the higher peak emissions during periods of rewetting and thawing observed in 2007.

Since N₂O flux was not measured in the crop field mid April to mid May 2006, and fertilizer was applied and it rained during this period (Fig. 4A), we might have missed peak N₂O flux in response to rainfall after fertilizer application (Parkin and Kaspar, 2006; Baggs et al., 2003; Sehy et al., 2003). Also since N₂O flux was not measured in the crop field in August and September to October in the crop field 2006 (Fig. 4A), and there were several rewetting events during the periods, we might have missed peak emissions in the periods. It is suspected that these missed peak emissions may result in lower annual N₂O emission in the crop field 2006.

Many future climate change scenarios predict more severe droughts associated with summer drying and intense precipitation in a future warmer climate (Easterling et al., 2000; Wang, 2005; Burke et al., 2006; Meehl et al., 2006; Rowell and Jones, 2006; Alexander et al., 2006; Sillmann and Roeckner, 2008). Also the increase in freeze and thaw frequency (Gu et al., 2008) and the increased impacts on the area and depth of permafrost regions (Lawrence and Slater, 2005) are predicted in a future warmer climate. The observed peak N₂O emissions during the thawing of frozen soils and rewetting of dry soils in the crop field 2007 have important implications for greenhouse gas emissions in a changing climate which predicts a greater frequency of such conditions.

The observed large difference between measured N₂O emission and estimated N₂O emission by IPCC method (2006) (87% underestimation by IPCC method) suggests

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that the current IPCC (2006) N₂O emission estimation methodology, based on N input information, may underestimate emissions in the regions where soil rewetting and thawing are common. Additional studies are warranted to clarify the relationships between antecedent soil moisture/soil temperature and the frequency of dry-wet/frozen-thawed cycles and their subsequent effect on soil N₂O flux. The resulting improvements in N₂O emission models would improve the accuracy of the N balance of terrestrial ecosystems and improve predictions of the probable impacts of anthropogenic climate change on such factors as an increased risk of drought (e.g. Alexander et al., 2006; Sillmann and Roeckner, 2008) and an increase in freeze and thaw frequency (Gu et al., 2008).

5 Conclusions

Annual N₂O emissions from soils within all riparian buffers (1.8 kg N₂O-N ha⁻¹ in 2006 and 3.4–4.5 kg N₂O-N ha⁻¹ in 2007) were significantly lower than within the cropped fields (7.2 kg N₂O-N ha⁻¹ in 2006 and 16.8 kg N₂O-N ha⁻¹ in 2007) and no differences were observed among the different kinds of riparian buffers. While N₂O peak emissions following the rewetting of dry soils and thawing of frozen soils contributed significantly to annual N₂O emission in the crop field, soils in riparian buffers were less sensitive to the events. Over a 2-year period, the EF of soils in riparian buffers (0.02) was about one third that of the crop field (0.07) with N input lower within soils in riparian buffers than in the crop field. Such findings indicate that even if riparian buffers were established for their water quality function (e.g. enhanced denitrification) throughout the watershed, they would only represent 1% of the annual N₂O emission. In addition, this study also suggests N input cannot always explain N₂O flux and that the N input-based IPCC methodology for estimating N₂O emissions may underestimate fluxes in the regions where with frequent rewetting of dry soils and thawing of frozen soils occurs. Additional studies characterizing N₂O peak emissions are needed to better understand annual N₂O fluxes and the N cycle within these systems, and to improve prediction of the

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impacts of future climate change.

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Table 1. Soil properties (mean \pm standard error) ($n=6-9$ except bulk density; $n=27$) of the sites. Soil samples (depth 0–15 cm) were collected in a forest buffer, a warm-season grass filter, a cool-season grass filter, and an adjacent crop field in October 2006 and September 2007.

Site	Soil texture†	Bulk density	pH	TC	TN	NH ₄ -N	NO ₃ -N
		mg m ⁻³		– g kg ⁻¹ soil –		– mg N kg ⁻¹ soil –	
Crop field	Loam	1.67 \pm 0.02a‡	5.9 \pm 0.1c	22.8 \pm 1.0c	1.9 \pm 0.1c	1.7 \pm 0.2b	1.2 \pm 0.5a
Forest buffer	Loam	1.10 \pm 0.03c	7.3 \pm 0.1a	42.9 \pm 3.2a	3.8 \pm 0.3a	4.1 \pm 0.6a	0.7 \pm 0.2a
Warm-season grass filter	Loam	1.29 \pm 0.05b	6.7 \pm 0.2b	29.1 \pm 2.7bc	2.6 \pm 0.2bc	3.9 \pm 0.5a	0.2 \pm 0.1a
Cool-season grass filter	Loam	1.19 \pm 0.04bc	6.9 \pm 0.1ab	32.4 \pm 1.6bc	2.9 \pm 0.1b	4.3 \pm 0.4a	0.9 \pm 0.3a

†Marquez et al. (2004).

‡Values in the same column followed by a different letter are significantly different ($P<0.05$).

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Table 2. Nitrogen inputs from crop residues ($n=5$), dead roots ($n=5$), and plant litter ($n=5$) of the previous year in the crop field and riparian buffers in 2006 and 2007 and estimated N inputs (IPCC 2006) from crop residues and dead roots of the previous year in the crop fields in 2006 and 2007.

Site	Measured N (kg N ha^{-1})				IPCC-Estimated N (kg N ha^{-1})		
	Crop residues	Dead roots§	Litter	Total	Crop residues§§	Dead roots§§	Total
Crop field (2006) †	53.1	29.0	–	82.1	42.4	14.0	56.4
Crop field (2007) ‡	61.2	31.0	–	92.2	73.4	44.9	118.3
Forest buffer (2006)	–	22.8	55.4	78.2	–	–	–
Warm-season grass filter (2006)	–	15.1	43.6	58.7	–	–	–
Cool-season grass filter (2006)	–	30.5	83.3	113.8	–	–	–
Average of riparian buffers (2006)	–	22.8	60.7	83.6	–	–	–
Forest buffer (2007)	–	22.8	66.9	89.8	–	–	–
Warm-season grass filter (2007)	–	15.1	30.3	45.4	–	–	–
Cool-season grass filter (2007)	–	30.5	41.2	71.8	–	–	–
Average of riparian buffers (2007)	–	22.8	46.2	69.0	–	–	–

†From soybeans.

‡From corn.

§N in dead roots (0 to 125 cm, fine and small root) was calculated from Tufekcioglu et al. (1999, 2000, 2003).

§§Used harvested annual dry matter (d.m.) yield: 3934.1 kg d.m. ha^{-1} (soybeans) in 2005 and 10 419.8 kg d.m. ha^{-1} (corn) in 2006.

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Table 3. Measured (Mea.) N inputs and N₂O emission, ratio of measured (Mea.) N₂O emission to N inputs, estimated (Est.) N₂O emission by IPCC 2006 method, and the ratio of measured (Mea.) N₂O emission to estimated (Est.) N₂O emission in the crop field and riparian buffers. Units of all N input and measured (Mea.) and estimated (Est.) N₂O-N is kg N ha⁻¹.

Crop field	N inputs [†]				Mea. N ₂ O-N	Mea. N ₂ O-N: N inputs	IPCC-Est. N ₂ O-N			Mea. N ₂ O-N: Est. N ₂ O-N
	Fertilizer‡	Crop residues & roots§	Deposition#	Total			Direct ††	Indirect ‡‡	Total	
2006	133.4	82.1	7.7	223.2	7.2	0.03	1.9	0.13	2.0	3.5
2007	–	92.2	7.7	99.9	16.8	0.17	1.2	–	1.2	14.2
2006–2007	133.4	174.3	15.4	323.1	24.0	0.07	3.1	0.13	3.2	7.5

Riparian buffers	N inputs					Mea. N ₂ O-N	Mea. N ₂ O-N: N inputs
	Litter & roots	Runoff §§	Ground water¶¶	Deposition#	Total		
2006	83.6	0.5	36.1	7.7	127.9	1.8	0.01
2007	69.0	6.0	36.1	7.7	118.8	4.0	0.03
2006–2007	152.6	6.5	72.2	15.4	246.7	5.8	0.02

†Biological N fixation was not included as a direct source of N₂O because of the lack of evidence of significant emissions arising from the fixation process itself (Rochette and Janzen, 2005; IPCC, 2006).

‡Pelletized urea (133.4 kg N ha⁻¹) was applied in the crop field (corn) in April 2006.

§From previous year.

§§In an event (>0.02 mm runoff), 0.5 kg N in run-off flowed from crop fields was retained in the riparian buffers (calculated from Lee et al., 2003). During 2006–2007, there were 13 events (>20 mm rainfall) in the sites.

¶¶Average of reduced N load in ground-water under two different riparian buffers (data from Kim et al., 2009).

Annual dry and wet deposition (ha⁻¹ y⁻¹) was 7.7 kg of N on the Iowa State University campus (19 km south of the study site) in January 2003–January 2004 (Anderson and Downing, 2006).

†† Annual amount of direct N₂O–N emissions produced from managed soils. Used harvested annual dry matter (d.m.) yield: 3934.1 kg d.m. ha⁻¹ (soybeans) in 2005 and 10 419.8 kg d.m. ha⁻¹ (corn) in 2006.

‡‡ Annual amount of N₂O–N produced from atmospheric deposition of N volatilized from managed soils.

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Table 4. The estimated N_2O emission in actual riparian buffers ($\text{N}_2\text{O}_{\text{RBa}}$), hypothetical riparian buffers ($\text{N}_2\text{O}_{\text{RBh}}$) and crop fields ($\text{N}_2\text{O}_{\text{CF}}$) in the Bear Creek watershed and the ratio between them. It is hypothesized that 30 m width riparian buffers are installed on the both side of the creek.

	unit	value
Area of current riparian buffers (RBa)	ha	75.9
Total length of Bear Creek	m	56 473
Width of riparian buffers	m	30†
Hypothetical area of riparian buffers (RBh)	ha	338.8
Total area of crop fields in the watershed	ha	6810
EF of riparian buffers (EF_{RB})	$\text{kg N}_2\text{O-N (kg N input)}^{-1}$	0.02
EF of crop fields (EF_{CF})	$\text{kg N}_2\text{O-N (kg N input)}^{-1}$	0.07
N input rate of riparian buffer	$\text{kg N ha}^{-1} \text{y}^{-1}$	123.4‡
N input rate of crop fields	$\text{kg N ha}^{-1} \text{y}^{-1}$	161.6§
N_2O emission in current riparian buffers ($\text{N}_2\text{O}_{\text{RBa}}$)	$\text{kg N ha}^{-1} \text{y}^{-1}$	187.2
N_2O emission in hypothetical riparian buffers ($\text{N}_2\text{O}_{\text{RBh}}$)	$\text{kg N ha}^{-1} \text{y}^{-1}$	835.9
N_2O emission in crop fields	$\text{kg N ha}^{-1} \text{y}^{-1}$	77 010.9
$\text{N}_2\text{O}_{\text{RBa}} / \text{N}_2\text{O}_{\text{CF}}$	$\text{kg N ha}^{-1} \text{y}^{-1} (\text{kg N ha}^{-1} \text{y}^{-1})^{-1}$	0.002
$\text{N}_2\text{O}_{\text{RBh}} / \text{N}_2\text{O}_{\text{CF}}$	$\text{kg N ha}^{-1} \text{y}^{-1} (\text{kg N ha}^{-1} \text{y}^{-1})^{-1}$	0.01

†Riparian buffers >30 m are recommended for fully effective nutrient reduction (Mayer et al., 2006).

‡Average of 2006–2007 ($246.7 \text{ kg N ha}^{-1}$) in riparian buffers.

§Average of 2006–2007 ($323.1 \text{ kg N ha}^{-1}$) in the crop field.

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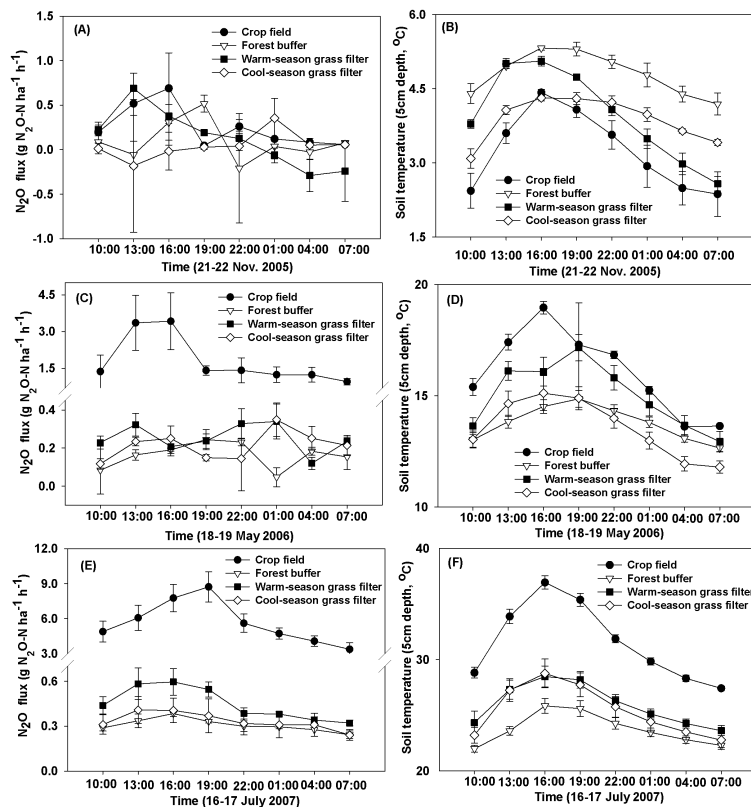


Fig. 1. Diel variation of N_2O flux and soil temperature (5 cm dept) in crop field, forest buffer, warm-season and cool-season grass filter in 21–22 November 2005 (A and B), 18–19 May 2006 (C and D), and 16–17 July 2007 (E and F). Observations are mean values with standard errors of the mean.

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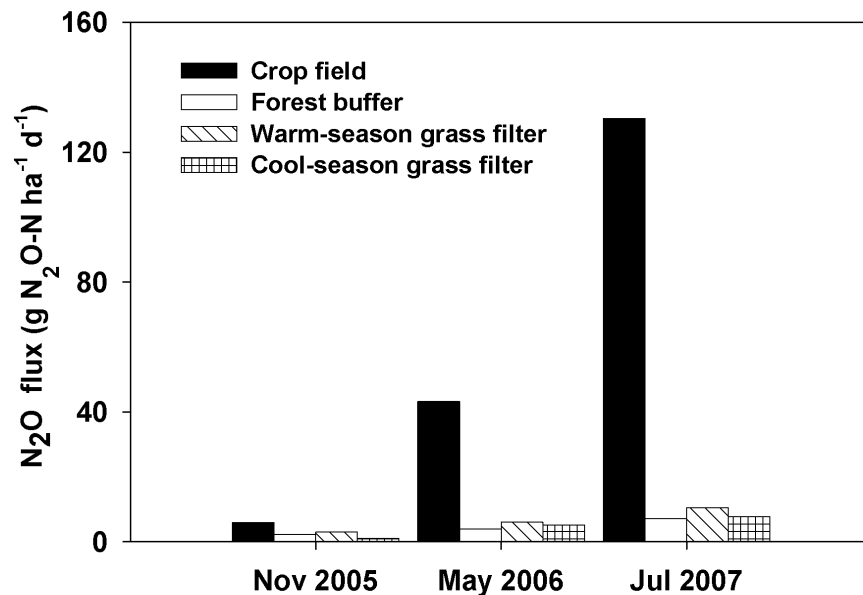


Fig. 2. Cumulative diel N_2O emission in crop field, forest buffer, warm-season and cool-season grass filter in 21–22 November 2005, 18–19 May 2006, and 16–17 July 2007.

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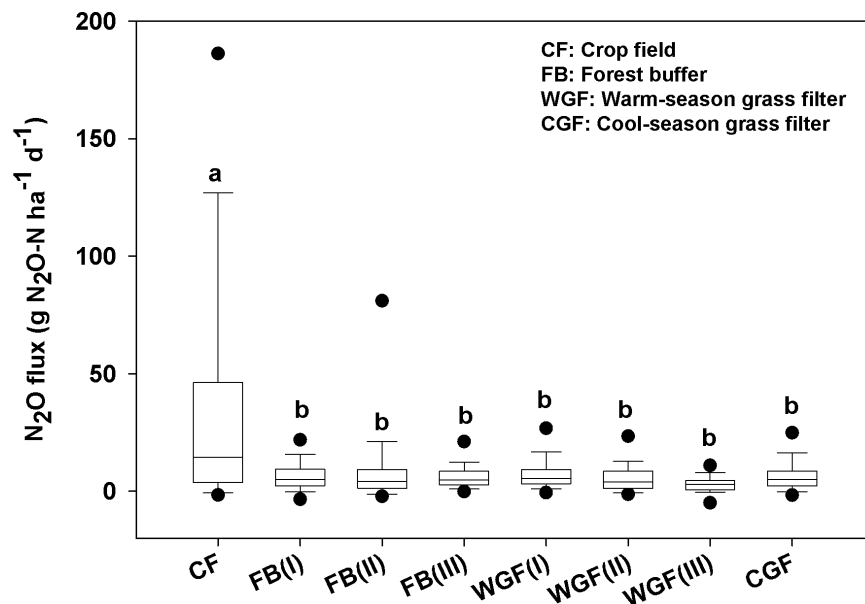


Fig. 3. Daily N_2O flux from soils within the crop field and riparian buffers in 2006 and 2007 ($n=72\text{--}93$). I, II, and III indicate replicates. The lower boundary of the box indicates the 25th percentile, the line within the box marks the median, and the upper boundary of the box indicates the 75th percentile. Error bars indicate the 90th and 10th percentiles. Solid circles indicate outliers.

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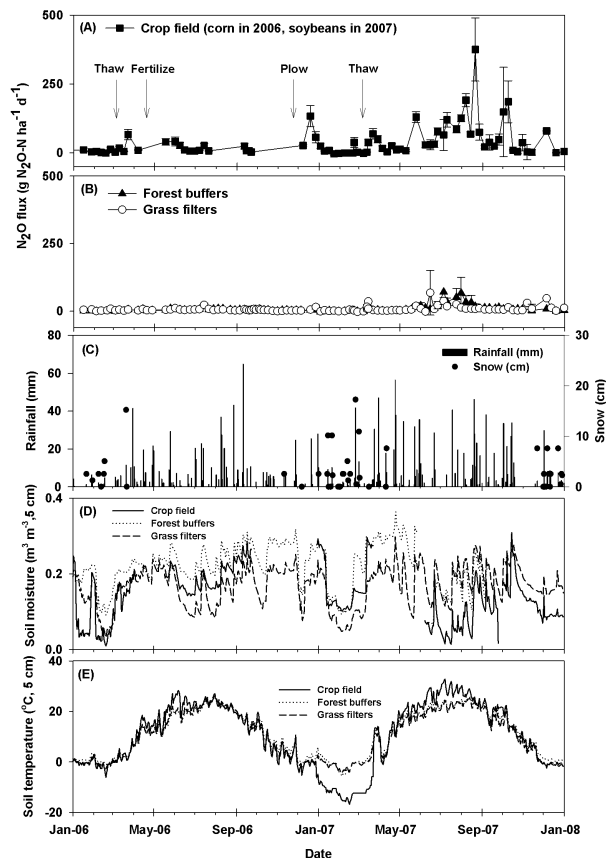


Fig. 4. Nitrous oxide emissions (A, B), precipitation (C), and daily average of soil moisture (D) and soil temperature (E) in forest buffers ($n=3$), grass filters ($n=4$), and adjacent crop field ($n=1$) during 2006 and 2007. Observations are mean values with standard errors of the mean in (A) and (B).

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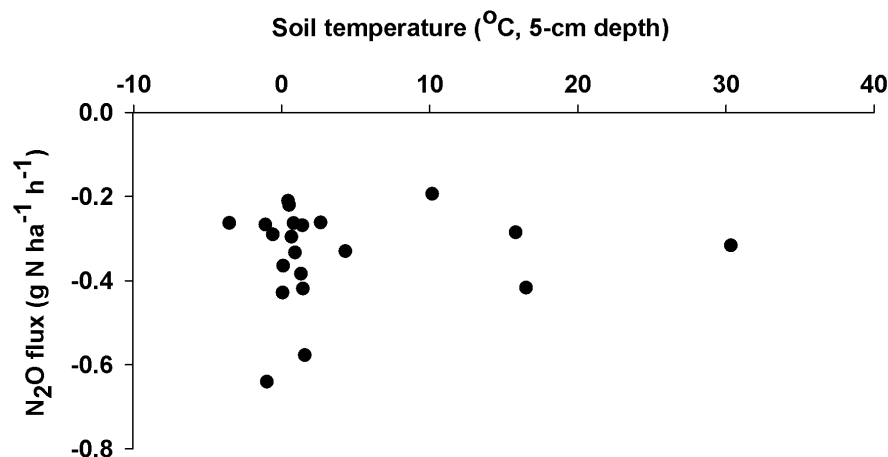


Fig. 5. Observed negative N₂O flux ($< -0.175 \text{ g N}_2\text{O-N ha}^{-1} \text{ h}^{-1}$, minimum detectable flux; significance was satisfied with 95% confidence limits) of the slope was tested and on-site soil temperature (5 cm depth) in forest buffers, grass filters, and adjacent crop field during 2006 and 2007.

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